

## METHOD OF TREATING CHEMICAL CELLULOSE PULP

### BACKGROUND AND SUMMARY OF THE INVENTION

The invention relates to a method of treating chemical cellulose pulp from an alkaline pulping process in a chlorine dioxide stage which includes an acid treatment at a temperature of over 80°C.

Pulp mills have recently attempted to avoid the use of elementary chlorine, and also minimize the use of chlorine dioxide, for environmental protection and marketing reasons. Disadvantages caused by elementary chlorine include both noticeable malodorous gaseous emissions and liquid effluents from chemical pulp mills into water systems. Liquid chlorine dioxide does not have odor problems on as large a scale as elemental chlorine, but it adversely affects water systems. When comparing these chlorine chemicals with each other by means of the AOX number designating the loading they incur on water systems, it is seen that elementary chlorine is many times more detrimental than chlorine dioxide. The AOX number of chlorine is of the order of 4 - 7 and that of chlorine dioxide is about 1 - 1.5, or even lower.

Therefore, sequences utilizing chlorine dioxide are still popular and environmentally feasible. There are many reasons for this. The price of chlorine dioxide is very competitive compared with that of other bleaching and delignifying chemicals. Also the strength and brightness of pulp obtained by dioxide bleaching are good, in fact at least approximately of the same order as those obtained by using peroxide at the same chemical consumption level (kg/admt).

Chlorine dioxide bleaching (D) is a well-known and widely used bleaching procedure. Conventional chlorine dioxide bleaching is usually performed at a temperature of 50 - 80°C and with a chlorine dioxide dosage of about 10 - 30 kg per ton of pulp. Typical sequences used are, for example, D<sub>0</sub>ED<sub>1</sub>ED<sub>2</sub> and OD<sub>0</sub>ED<sub>1</sub>ED<sub>2</sub> and modifications thereof. The treatment time in a D<sub>0</sub> stage is usually shorter than in other D stages, being for example, between about 30 - 90 minutes. The pH of the pulp decreases

to the range of 1 - 3 towards the end of the D<sub>0</sub> stage. In the D<sub>1</sub> and D<sub>2</sub> stages the treatment time is 2 - 3 hours and the pH a little higher than in the D<sub>0</sub> stage. The chlorine dioxide stage (all types) is usually performed at a temperature of about 70°C, while the treatment time in the D<sub>0</sub> stage is 0.5 - 2 hours and in the D<sub>1</sub> and D<sub>2</sub> stages 2 - 3 hours.

- 5 Higher temperatures than about 70°C have typically been avoided as the low final pH in the range of 1 - 3 in the D stage combined with a high temperature and long treatment time deteriorates the strength properties of the pulp fibers.

Other elemental-chlorine-free bleaching processes, such as those using peroxide and ozone, have also been introduced. As pulp bleached with chlorine dioxide has good properties, the development of ClO<sub>2</sub> bleaching has been continued in conjunction with other elemental chlorine-free processes. One of the most important objects is to reduce the amount of chlorine dioxide needed in bleaching and thus to make ClO<sub>2</sub> bleaching more environmentally acceptable.

- 10 Finnish patent application no. 944808 and WO publication no. 96/12063 disclose an acid treatment (A), also known as a hot acid step, method for pulp by which the consumption of chlorine dioxide can be reduced. This treatment removes hexenuronic acids, which can react with chlorine dioxide and thus increase chemical consumption, from the pulp. The acids may be removed by adjusting the pH of the pulp to the range of 2 - 5, preferably between 2.5 - 4, and treating at a temperature of over 80°C, preferably between 15 90 - 110°C, at a time between 30 - 300 minutes. During acid treatment the kappa number of the pulp is typically reduced by 2 - 9 units. When the sequence O-A-D-E-D is used, the consumption of chlorine dioxide in the bleaching of hard wood pulp has reduced by 30 - 20 40% at a brightness of ISO 88%. The corresponding consumption with soft wood pulp has reduced by 10 - 20%. In both cases, the yield remains nearly unchanged compared with 25 bleaching without an acid (A) stage.

The present invention provides an alternative method of combining a hot acid step with a bleaching sequence utilizing chlorine dioxide. The invention provides a method which may be practiced in an economical manner, particularly in bleaching plants of

existing pulp mills. In other words, the invention is capable of fitting chlorine dioxide bleaching of pulp into a bleaching plant in an overall economical and environmentally acceptable manner.

The method of the invention is characterized in that the chlorine dioxide stage comprises successively at least a first chlorine dioxide step, and an acid treatment step, and that the pH of the first chlorine dioxide step is adjusted so that the final pH of the pulp in the first chlorine dioxide step is over 4. The conditions during the first chlorine dioxide step are such that the hexenuronic acid groups in the pulp do not react with chlorine dioxide.

As discussed above, it is known that hexenuronic acid groups are removed by hot acid treatment prior to chlorine dioxide treatment. According to the invention it has now been discovered that the  $\text{ClO}_2$  treatment can also be performed in a bleaching sequence before the hot acid treatment if reactions between the hexenuronic acid groups of the pulp and the chlorine dioxide are prevented. Thus, a D stage may comprise, successively, a D step and an A step. According to the method of the invention, the chlorine dioxide step of the DA stage is performed so as to have a final pH of over 4, preferably over 5. The highest desirable pH value at the end of the first  $\text{ClO}_2$  step is normally about 7.

Conventionally, the final pH of the first or the second chlorine dioxide bleaching stage is less than 4, typically 1 - 3.5. Surprisingly, it has been found out that hexenuronic acids do not react with chlorine dioxide at the pH range of over 4 and thus no chemical is consumed by reactions with chlorine dioxide. Chlorine dioxide is reduced to chlorite but it does not decompose further. The chlorine dioxide dose in this step is about 0.1 - 1.5% active Cl (1 - 15 kg active Cl/admt), preferably between about 0.5 - 1.0% active Cl (5 - 10 kg active Cl/admt).

In the acid treatment (A) step, the conditions are typically as follows:

- pH 2 - 5, preferably between 2.5 - 4;
- temperature over  $80^\circ\text{C}$ , preferably between  $90 - 110^\circ\text{C}$ ; and
- time 30 - 300 minutes, preferably at least t minutes, where

$t = 0.5 \exp(10517/(T+273) - 24)$  ( $t = 0.5 e^{((10517/(T+273)) - 24)}$ ), in which  $T$  ( $^{\circ}\text{C}$ ) is the temperature of the acid treatment.

According to the invention, the temperature in the D step of the DA stage is preferably over  $70^{\circ}\text{C}$ , preferably over  $75^{\circ}\text{C}$ , most preferably between  $80 - 100^{\circ}\text{C}$ , which is higher than the temperature of a conventional D stage. Thus, the temperature in the D and the A steps is essentially the same and there is no special need to cool or to heat the pulp between the steps, which is advantageous for energy economy. However, the invention is not limited to high temperature in the D step, but rather the D step may also be performed at the conventional D step temperature of below  $70^{\circ}\text{C}$ .

The treatment time in the D step of the invention is short, less than 10 minutes, preferably 30 seconds to 3 minutes. Conventionally, the chlorine dioxide treatment time is over 30 minutes, even 120 minutes depending on the temperature and therefore a conventional D step requires its own reactor. The DA stage according to the invention may be practiced by performing the acid treatment in a reactor tower but because of the short retention time the D step preceding the A step may take place, for example, in the feed line of the A step tower. The pulp flowing in the line is heated to the desired temperature, for example about  $90^{\circ}\text{C}$ , and chemicals, such as chlorine dioxide, and alkali or acid if necessary to adjust the pH, are mixed into the pulp. The pulp flows under these conditions for the required period, e.g. one minute, and subsequently, acid is added to the pulp and it is supplied into the acid tower.

By providing chlorine dioxide treatment before acid treatment according to the invention, the acid demand in the A step is reduced as the reactions of chlorine dioxide with the pulp lignin produce hydrochloric acid and organic acids as byproducts.

It is characteristic of a preferred embodiment of the invention that the chlorine dioxide stage as described above comprises in addition to the D and A steps described above a second D step, i.e. the chlorine dioxide stage comprises a first chlorine dioxide step, then a hot acid treatment step, and then a second chlorine dioxide step (DAD, or D/A/D). The second  $\text{ClO}_2$  step is performed in acidic conditions, in other words the pH may be less than 2 but preferably is between 2 - 4. Thus, no special adjustment of the pH

is needed after the A step. Adjustment of the temperature is not necessary, either, but rather the entire chlorine dioxide stage may be practiced essentially at the same temperature as the A step, and no special adjustments of the temperature are needed between the steps.

5 The treatment time in the second D step is preferably also short, less than 10 minutes, preferably 1 - 5 minutes, and it may be performed for example in the discharge line of the A step tower prior to the washer following the DAD stage. Chlorine dioxide is added to the pulp flowing in the discharge line and the temperature and the pH are adjusted if necessary. The required chlorine dioxide dose is typically 0.5 - 2.0% active Cl (5 - 20 kg active Cl/admt). The acid treatment removes hexenuronic acids from the pulp and therefore the amount of chlorine dioxide chemical required in the second  $\text{ClO}_2$  step is smaller than with pulp from which hexenuronic acids have not been removed.

10 In the (DAD) embodiment of the invention, the chlorine dioxide treatment may be considered to have been divided into two relatively short partial treatments. Both steps may be practiced at a high temperature; therefore the temperature and the treatment time must be chosen so as to cause as little viscosity loss in the pulp as possible. Two partial treatments contribute to a more homogenous brightness of the pulp than a single longer treatment.

15 The DA stage may be also practiced by chelating the pulp with EDTA, DTPA or a corresponding compound, after the A step in order to remove harmful metals; i.e. a DAQ stage may be utilized. Providing a chelating treatment in connection with the DA stage is advantageous particularly if the bleaching sequence comprises a later bleaching stage with a chemical such as peroxide which is adversely affected by heavy metals. The Q step may be performed at essentially the same temperature as the preceding D and A steps.

20 The pH may be in the range of 3 - 6.

25 The total amount of chlorine dioxide needed in the DA stage is not greater than the amount needed in an AD stage although the first D step is performed before the acid treatment. The final pH of over 4 in the first D step prevents reactions between chlorine dioxide and hexenuronic acids. A DA stage has produced pulp of at least as good quality

as an AD stage. An advantage provided by a DA stage, or a DAD stage, is that, compared with an AD stage, a DA or a DAD stage may be effected with simpler apparatus as each step does not require its own tower. However, the invention may also be practiced so that one or both of the D steps are performed in towers of their own.

5 A disadvantage of the AD stage may be the release of malodorous gases in the acid step if the pulp after washing still contains adequate amounts of sulfur compounds from digestion. When the D step precedes the A step, malodorous gases are oxidized by the bleaching chemical during the DA stage.

10 The method of the invention is applicable to chemical cellulose pulps manufactured by the sulfate process and other alkaline methods, which pulps typically contain hexenuronic acid compounds. The pulp to be treated has preferably been oxygen delignified after digestion and before the chlorine dioxide stage. The DA stage according to the invention may be at the beginning of the bleaching sequence, for example after oxygen delignification, or later in the sequence, for example after a peroxide stage.  
15 Therefore the invention is advantageously applied for example in connection with the following treatment/bleaching sequences or partial treatment/bleaching sequences:

digestion - O - DAD - E;

digestion - O - DAD - E - DN - D; or

digestion - O - Q - OP - D/A/Q - PO,

20 in which:

"-" indicates a wash between the stages,

"O" indicates a delignification stage utilizing at least oxygen,

"Q" indicates removal of metals by chelating,

"A" indicates a hot acid treatment as described above,

25 "E" indicates an alkaline bleaching stage, and

"OP" or "PO" indicate a bleaching stage based on oxygen and/or peroxide, possibly at least part of the steps being pressurized and O indicating oxygen chemical and P peroxide, and the first letter in each step signifying the main effective bleaching

chemical and the second letter, when used, designating a bleaching chemical supporting the bleaching reaction.

According to one aspect of the present invention a method of treating chemical cellulose pulp from an alkaline pulping process (e.g. the kraft process) in a chlorine dioxide stage is provided. The method comprises: (a) In the chlorine dioxide stage, bleaching the chemical cellulose pulp in a first chlorine dioxide step, and adjusting the pH of the pulp in the first chlorine dioxide step so that the final pH of the step is over 4. And then, (b) in the chlorine dioxide stage effecting an acid treatment of the chemical cellulose pulp at a pH of between 2 – 5 and at a temperature of over 80°C. Preferably (a) is practiced so that the final pH of the first chlorine dioxide step is over 5, and so that hexenuronic acid groups in the pulp substantially do not react with chlorine dioxide. In the method (a) is also preferably further practiced so that the temperature in the first chlorine dioxide stage is over 70°C, preferably over 75°C, and most preferably between about 80-100°C. Also (a) is further practiced so that the treatment time in the first chlorine dioxide step is less than ten minutes, preferably between 30 seconds-3 minutes. The chlorine dioxide dosage during the practice of (a) is preferably between about 0.5-1.5% active chlorine.

Also preferably (b) is practiced so that the pH is between 2.5-4, the temperature is between 90-110°C, and the time is between 30-300 minutes, preferably pursuant to the formula described above. Since (a) and (b) are in the same stage there is no intermediate (i.e. between step) washing.

Following (b) the method preferably further comprises (c) bleaching the chemical cellulose pulp, after (b), in a second chlorine dioxide step. Preferably (a)-(c) are practiced so that the treatment temperatures in the first chlorine dioxide step, the acid treatment step, and the second chlorine dioxide step, are substantially the same (between about 90-100°C, e.g. about 95°C). During the second chlorine dioxide step the treatment dosage is preferably between about 0.5-2.0%, and the temperature and time parameters are substantially the same as for the first chlorine dioxide step.

The method may also further comprise (d) treating the chemical cellulose pulp with chelating agent (such as EDTA, DTPA, mixtures thereof, or other chelating agents) after

(a) and (b), especially if further treatment of the pulp is to be provided in a peroxide or other bleaching stage sensitive to the presence of metals. Also all of steps (a) through (c) may be practiced in a line leading up to an acid tower, in the acid tower, and in a line leading from the acid tower to a washer. All of the steps DAD of the stage are of course  
5 practiced without between step washing, inherent in the fact that they are part of the same stage.

It is the primary object of the present invention to provide for the advantageous treatment of chemical cellulose pulp from alkaline pulping processes with chlorine dioxide so as to minimize the use of chlorine dioxide, minimize the amount and expense of  
10 equipment necessary, enhance the energy economy of the process, and minimize the release of malodorous gases, such as sulfur compounds. This and other objects of the invention will become clear from an inspection of the detailed description of the invention, and from the appended claims.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

15 FIGURE 1 schematically illustrates by way of example a preferred apparatus for carrying out the method of a preferred embodiment of the invention, that is treating cellulose chemical pulp from an alkaline process in a DAD stage.

#### **DETAILED DESCRIPTION OF THE DRAWINGS**

20 In the exemplary embodiment of FIGURE 1, chemical cellulose pulp, e.g. produced by kraft pulping, is transferred from a preceding treatment stage 10 by a high consistency pump 12 to an acid tower 18. The consistency of the pumped pulp is between about 6 - 25%, preferably between about 8 - 18%. The preceding stage 10 may be a wash stage following digestion, or more often an oxygen delignification stage following digestion, or a wash following oxygen delignification.

25 Alkali or acid is added to the pulp in order to adjust the initial pH for the chlorine dioxide treatment or the first D step so that the final pH is over 4, preferably over 5, in order to prevent reactions between chlorine dioxide and hexenuronic acids. The alkali and



the chlorine dioxide may be added directly to the pump 12 as schematically illustrated in FIGURE 1, or may be injected into duct 15 between the pump 12 and the tower 18, or added to a conventional mixer 14 provided for this purpose. The typical chlorine dioxide dosage added (e.g. at 12) is between about 0.5 -1.5% active Cl.

5           Steam is preferably added to the pulp in order to raise the temperature typically up to 80 - 100°C. Steam may be added prior to the pump 12 in a conventional steam mixer (not illustrated) or mixed in the duct 15 following the pump 12. Alternatively, the pulp may be heated indirectly in the duct 15 by a conventional heat exchanger (not shown).

10           Thus, the first D step is performed in the feed line 15 of the acid tower 18 while the pulp flows in the line 15. The treatment time in this step is typically between 30 seconds to 3 minutes.

15           The first D step is followed by an acid treatment in the tower 18. After the chlorine dioxide treatment the pH of the pulp is adjusted (e.g. decreased), if necessary, to the level 2 - 5 required by the acid treatment in 18 by adding acid (sulfur acid, hydrochloric acid, waste acid from the production of chlorine dioxide, or any suitable organic acid) to the pulp in the mixer 14. Also the temperature may be adjusted if necessary but according to the invention all the steps of the DAD stage are preferably practiced at about the same temperature, for example about 95°C, so that no special temperature adjustment is required between the steps.

20           The feed and flow of pulp to the acid tower 18 should be as even as possible by using a conventional distributor 16 or a doctor. The distributor 16 is preferably as disclosed, for example, in U.S. patent no. 4,964,950, and its use for the above purpose is described in Finnish patent publication no. 94442. If the device 16 has adequate mixing properties and if desired, acid may be added to the device 16 and thus even avoid the  
25           use/purchase of the mixer 14.

          Pulp flows from the device 16 to the reactor tank 18 dimensioned for the treatment time required by the acid treatment step A, for example 120 minutes at 95°C. Using a distributing feeder 16 as described in FI publication no. 94442, all portions of the tower 18 are filled evenly and the pulp column rises up evenly in the tower 18 so that harmful

channeling cannot occur. Correspondingly, the top of the tower 18 is provided with a conventional discharger 20 or a discharge doctor to guide pulp to the discharge line 24 of the tower.

The second D step is performed in the discharge line 24 from tower 18 in order to bleach the pulp. Chlorine dioxide may be added to the pulp via the acid tower discharger 20 or to a pump 22 in the discharge line 24. Also a separate mixer (not illustrated) may be provided in the line 24 for addition of chemical, preferably between 0.5 - 2.0% active Cl.

The addition of chemicals to the pulp is effected so that a proper treatment time for carrying out the second D step in the discharge line 24 is provided before the conventional washer 26 is reached. The retention time is less than 10 minutes, preferably between about 1 - 5 minutes. The treatment temperature of the second D step is preferably the same as that of the first D and A steps; thus no special adjustment of the temperature after the A step is needed here either. If desired, pulp may be heated or cooled in a conventional heat exchanger (not shown) or by direct feeding of steam. A higher temperature (e.g. between about 75-110°C) than conventionally is, however, required in order to obtain adequate bleaching during the short treatment time in line 24.

The pH of the second D step is lower than that of the first D step. Typically the pH of the second D step in line 24 is between about 2 - 4; thus adjustment of the pH is usually not needed after the A step. If necessary, the chemical adjusting the pH may be added at the same time and place as the chlorine dioxide (e.g. in discharger 20).

Pulp was bleached in a DAD stage in the manner described above and subsequently the pulp was washed in the washer 26 and transported to further treatment. Typically the further treatment (subsequent stage) is an E stage. The results of one example of this treatment are:

#### Example

Oxygen-bleached initial pulp was tested in a laboratory, the kappa number of which was 11.9, viscosity 1061 ml/g and the ISO brightness 49.2%. The pulp was treated with the following sequences:

1. DAD - E<sub>O</sub> - D<sub>N</sub> - D

D: - ClO<sub>2</sub> dose 1.0% as active Cl

- time 1 minute

- final pH 5.3

- temperature 95°C

5

A: - time 180 minutes

- pH 3.5

- temperature 95°C

D: - ClO<sub>2</sub> dose 1.25% as active Cl

- time 2 minutes

- final pH 2.5

- temperature 95°C

10

E<sub>0</sub> - 85°C, 60 minutes, 1.25% NaOH, O<sub>2</sub> 4 bar, final pH 11.7

- kappa number after treatment 2.3

- viscosity after treatment 890 mg/l

- brightness after treatment 70.2% ISO

15

D<sub>N</sub> - 75°C, 180 minutes, 1.8% ClO<sub>2</sub> as active Cl, 0.3% NaOH, final pH 3.3

- N (neutralization) pH 8.3

D - 75°C, 180 minutes, 0.8% ClO<sub>2</sub> as active Cl, 0.1% NaOH, final pH 5.1

The final bleached pulp had a viscosity of 868 ml/g, and a brightness of 89.9% ISO

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In the second test the same initial pulp was treated

## 2. AD - E<sub>0</sub> - D<sub>N</sub> - D

A: - time 180 minutes

- pH 3.5

- temperature 95°C

25

D: - ClO<sub>2</sub> dose 2.25% as active Cl

- time 1 minute

- final pH 2.1

- temperature 95°C

E<sub>O</sub> - 85°C, 60 minutes, 1.25% NaOH, O<sub>2</sub> 4 bar, final pH 11.6

- kappa number after treatment 2.7

- viscosity after treatment 890 mg/l

- brightness after treatment 69.4% ISO

5 D<sub>N</sub> -75°C, 180 minutes, 1.8% ClO<sub>2</sub> as active Cl, 0.3% NaOH, final pH 3.4

- N (neutralization) pH 8.3

D - 75°C, 180 minutes, 0.8% ClO<sub>2</sub> as active Cl, 0.1% NaOH, final pH 5.1

The final bleached pulp had a viscosity of 866 ml/g, and a brightness of 89.9% ISO.

Based on the above example it may be concluded that a <sup>a conventional AD</sup> ~~DA~~ stage and an <sup>a DA</sup> ~~AD~~ stage

10 according to the invention produce pulp of the same quality. Some practical advantages described above may be obtained by effecting the chlorine dioxide and the acid treatment according to the invention as compared with an AD sequence.

15 In all of the above descriptions all narrower ranges within a broad range are also specifically provided. For example the temperature range of 80-100°C includes 81-95°C, 94-99°C, and all other narrower ranges within the broad range.

20 While the invention has been herein shown and described in what is presently conceived to be the most practical and preferred embodiment, it will be apparent to those of ordinary skill in the art that many modifications may be made thereof within the scope of the invention, which scope is to be accorded the broadest interpretation of the appended claims so as to encompass all equivalent methods.